



# Materials challenges and technical approaches for realizing inexpensive and robust iron–air batteries for large-scale energy storage

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## ABSTRACT

A high performance iron–air rechargeable battery has the potential of meeting the requirements of grid-scale energy storage. When successfully demonstrated, this battery technology can be transformational because of the extremely low cost of iron, the extraordinary environmental friendliness of iron and air, and the abundance of raw materials. The key technical challenges that hinder the successful commercialization of the iron–air battery are its efficiency and cycle life. An innovative multi-pronged strategy that aims at raising the round-trip energy efficiency from 50% to 80%, and the cycle life from 2000 to 5000 cycles is therefore necessary to meet the requirements of large scale energy storage.

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## 1. Introduction

Large-scale electrical energy storage systems are needed to support an electricity grid as the fraction of renewable energy generation from sources such as solar and wind energy increases. The variability and intermittency in electricity generation from solar and wind sources are stochastic and aperiodic [1,2]. Consequently, buffering these unpredictable periods of energy generation with energy storage systems is critical to preserving the power quality of electricity and meeting the electricity demand.

The four principal requirements for such energy storage systems are scalability, low life-cycle cost, high efficiency, and fast response time. Electrochemical energy storage systems have the potential to meet these requirements, without the constraints of siting and geography required by other systems such as compressed air storage and pumped water storage. Electrochemical energy storage systems can also be used in conjunction with other systems in a hybrid mode as needed.

The United States Department of Energy has quantified the primary requirements for grid-scale electrical energy storage and launched a program to support the development of new technologies [3]. The economic targets are \$ 100/kWh for capital cost amortized over a

15-year period and an operating energy cost of no more than \$0.025/kWh. A battery life of 5000 charge–discharge cycles is required at a round-trip energy efficiency of 80% or greater. These requirements for cost and life are starkly different from electrical energy storage for vehicular transportation. Further, since the large-scale grid systems are stationary, the emphasis is not on high specific energy or energy density, although the energy density values translate indirectly into the overall cost of energy storage.

The goal of increasing the renewable energy generation from solar and wind to 30% of the United States' total electricity production by 2030 will require approximately 2000 GWh of energy storage capacity to be in place. This is an unprecedented level of electrical energy storage and will require inexpensive and robust technologies.

Electrochemical energy storage usually refers to rechargeable batteries and electrochemical capacitors. Rechargeable batteries can usually store ten to fifty times the energy of electrochemical capacitors per unit mass or volume of the system. However, electrochemical capacitors can deliver energy at ten to hundred times the rate that batteries are capable of. Therefore, a hybrid power system based on batteries and electrochemical capacitors would be ideal for simultaneously meeting the time response requirement of large-scale energy storage systems.

A comparison of the major advantages and disadvantages (Table 1) for various battery systems shows that none of the existing technologies can meet the cost and lifetime requirements [4]. Our

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**Table 1**

Comparison of the advantages and disadvantages of various battery systems for large-scale energy storage.

Battery system	Features/advantages	Major disadvantages
Zinc–bromine flow battery	Moderate energy density (65 Wh/kg), 1250 cycles, Moderate efficiency (70%), fairly mature technology with large units demonstrated.	Moderate to high cost (> \$150–\$200/kWh), Cycle life and efficiency needs to be improved.
Vanadium Flow Battery	3000 cycles, Moderate-to-high round-trip efficiency(85%) fairly mature technology that has been scaled up to 1 MWh	High cost(>\$500/kWh), toxic materials, relatively rare materials are used
Lithium–Ion Rechargeable	High energy density and high power density (100–200 Wh/kg), 1000 cycles, High round-trip efficiency (90%).	Very high cost (>\$1000/kWh), safety and abuse tolerance is low, cycle life needs to be improved.
Sodium–Sulfur	High Energy density (100–150 Wh/kg), 1500–3000 cycles, Moderate to high round-trip efficiency (80%).	Moderate–High Cost (\$200–300/kWh), High Temperature operation (300°–350 °C), requires thermal management systems.
Regenerative Fuel Cells	High Energy Density (400–600 Wh/kg), High Power Density, 2000 cycles	High cost (>\$1000/kWh), Efficiency is low (50%), and cycle life needs to be increased.
Nickel–Metal Hydride	Moderate energy density (60 Wh/kg), High power density, 1000 cycles	High cost (>\$450/kWh). Cycle life under deep discharge is low. Mature technology unlikely to see further improvement.
Iron–Air	Moderate Energy Density (50–75 Wh/kg), 2000 cycles, Low cost (<\$100/kWh), environmentally friendly, abundant raw materials, easily scalable.	Efficiency needs improvement (50% to 80%) and cycle life needs to be improved from 2000 to 5000 cycles .

comparison reveals that the iron–air battery stands out as a promising candidate because of its low cost, sustainability, and environmental friendliness. With improved efficiency and cycle life, the iron–air battery will be viable battery for large-scale energy storage.

In this paper we discuss the challenges with the iron–air battery for large-scale energy storage systems and describe the specific technical issues that need to be resolved. The objectives of this paper are: (i) to inform the reader of the emerging challenge of grid-scale energy storage and the relevant technical and cost requirements, (ii) describe how the iron–air battery presents a promising opportunity for development (iii) describe the technical issues to be addressed and (iv) outline some innovative approaches to resolution of the technical issues.

## 2. Factors affecting cost and performance of battery-based electrical energy storage

The cost of a battery is determined by various aspects of the technology: material availability, manufacturing cost, efficiency, cycle life under deep discharge conditions, safety requirements, and auxiliary systems needed. All these factors will have to be considered simultaneously in selecting a battery technology for development [4].

From Table 2 we conclude that of all the materials under consideration for large scale battery storage, iron is the most abundant, least expensive and practically non-toxic. While air is free, carbon dioxide-free air is needed for maintaining the lifetime of the batteries. Removing carbon dioxide from air will involve additional cost in scrubbing systems.

Sodium–sulfur based batteries are also quite promising from a materials cost and abundance standpoint. The sodium–sulfur battery that operates at 350 °C could present a limitation to the maintenance and extensive deployment of large systems. Also, the manufacturing techniques for such high temperature batteries that require hermetic

sealing can be quite expensive [5]. The sodium–metal chloride battery (ZEBRA) operates at a lower temperature than the sodium–sulfur battery. While the ZEBRA battery is somewhat safer than the sodium–sulfur battery, the use of expensive materials such as nickel and aluminum chloride makes the cost goal a challenge. Zinc/Bromine is the next system that is attractive from a cost standpoint. However, liquid bromine is quite toxic. Based on the escalating requirement for energy storage in the next 30 years, battery materials for which our reserves are less than 100 million metric tons are in the danger of being unsustainable. Further, geo-political control of resources must also be considered in the choice.

The iron electrode can be fabricated by low-cost pressed plate technology or by slightly more expensive sinter plate technology (developed formerly by Westinghouse Corporation in the early 1980s). The cells are not required to be completely sealed, on the contrary during normal operation the electrolyte must be circulated and the gasses must be vented. Iron electrodes may be fabricated from pure iron or oxide materials that are significantly cheaper than all battery materials in use today. Based on our preliminary estimate of the cost of the various components that constitute the iron–air battery for grid-scale applications (Table 3) the goal of capital cost of \$100/kWh is well within the reach for this technology. Thus, the manufacturing and fabrication of the iron–air battery stand out as a commercially attractive enterprise [6].

Round trip efficiency affects the size of battery required for energy storage. Most rechargeable batteries have a round-trip efficiency in the range of 85–95%. Efficiency losses arise from voltage losses during charge and discharge, occurrence of parasitic faradaic processes and self-discharge. Efficiency decreases as the rate of charge and discharge is increased. Consequently, to preserve efficiency the size of the battery must be increased or the cell design must be altered to reduce energy losses.

In redox flow batteries such as the vanadium redox battery the sizing of the electrodes is not coupled to the amount of electroactive

**Table 2**

Materials cost, reserves and toxicity.

Battery material	Cost, US \$/kg	Global resource reserves, million tons*	Toxicity
Zinc	2.2	150	Moderate to high
Lead	2.2	95	High
Vanadium	27	38	High
Chromium	10	1.8	High
Bromine	0.6	15,000 as sodium bromide	High
Sodium	1.7	10E10	None
Sulfur	0.20	1000	Moderate to low
Iron	0.20	100,000 as iron ore	None
Air (oxygen)	"Almost free"	Unlimited	None

\* Data from United States Geological Society Survey.

**Table 3**

Preliminary estimate of cost of components of the iron–air battery.

Component	US \$/kWh
Iron material	2
Grid cost	12
Cathode cost	12
Electrolyte	5
Water	5
Case	5
Pumps	15
Carbon dioxide management	2
Connectors and bus bars	1
Total	\$59/kWh

materials needed for energy storage. This is because the electroactive materials are stored in separate tanks outside the cell stack and are supplied to the cell stack for power generation. The iron–air battery like other metal–air batteries also has a similar advantage that at least at the air electrode – air flow sustains the oxygen electrode reaction, and no tanks are needed for storage of this reactant. The iron electrode is a standard battery electrode configuration with active materials that form the electrode and can be discharged at moderate rates of discharge.

The iron electrode however suffers from a low faradaic efficiency which must be addressed [7]. While most metal–air batteries that are commercial are not rechargeable, for the large-scale energy storage application the air electrode needs to be bi-functional in that it should sustain the oxygen reduction reaction during discharge and the oxygen evolution reaction during charge. Voltage losses at the air electrode during charge and discharge are dependent on the selection of suitable electrocatalysts.

Cycle life or durability of batteries has a direct impact on capital cost. Deep discharge cycling is required to minimize the size of the battery and allow for maximum utilization of active materials. However, deep discharge cycling reduces cycle life. Thus, batteries that can provide long cycle life at a high-level of material utilization are required. The iron electrode cycling between iron and iron(II) hydroxide provides long cycle life under deep discharge and at 400 Ah/kg, a high level of utilization. The iron electrode was originally developed for nickel–iron batteries that are famed for a 30 year life under deep-discharge conditions [8].

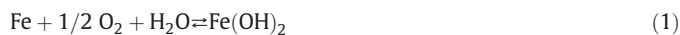
The bi-functional air electrode of an iron–air battery is much like a redox flow battery electrode in that the cycling degradation is associated with the duration of operation and not the extent of cycling. Degradation occurs by oxidation of the carbon substrate used for dispersing the catalysts. A substrate that resists oxidation during the oxygen evolution process will allow us to realize a robust air electrode. Lead–acid batteries are notorious for their poor cycle life upon deep discharge cycling. Redox flow batteries have the advantage of using electro-active materials in solution and thus do not degrade much with cycling. Electrodes based on zinc suffer shape change with cycling and this problem becomes a limitation after a few hundred cycles. Sodium–sulfur batteries have a long cycle life if they are kept at the operating temperature of 400 °C without thermal cycling.

The Westinghouse Corporation, the Swedish National Development Corporation and others avidly pursued the development of the iron–air battery during the mid-1970s and early 1980s for use in electric vehicles [9–11], however, the energy density and power density of these batteries did not reach the desired targets set for electric vehicle applications. Although, this technology did not meet the needs of vehicular applications, the **advantages** of the iron–air battery, for grid-scale applications are **compelling** based on above considerations of cost, performance and material properties. For this reason, we have directed our research efforts at understanding the technical issues to be addressed in the iron–air battery for grid-scale electrical energy storage applications.

### 3. Performance of the iron–air battery

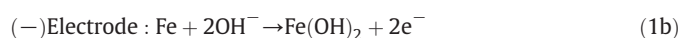
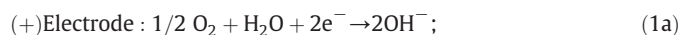
#### 3.1. Electrochemical reactions

The overall cell reaction in the iron–air battery that leads to generation of electrical energy is given by Eq. (1).

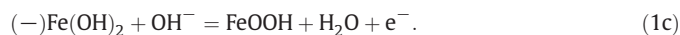


The backward reaction in Eq. (1) takes place during charging. The iron–air battery has an open circuit cell voltage of about 1.28 V and a theoretical energy density of 764 Wh/kg.

During discharge, iron on the negative electrode is oxidized to iron (II) hydroxide and oxygen is reduced at the positive electrode to form hydroxide ions. These processes are reversed during charging of the battery. The individual electrode reactions during discharge are given by:



Further discharge of the iron electrode beyond the two-electron step in Eq. (1b) will lead to the formation of iron oxyhydroxide or magnetite as per Eq. (1c)



The reaction in Eq. (1c) is kinetically less facile than the one given in Eq. (1b) and therefore discharging the iron beyond the  $\text{Fe}(\text{OH})_2$  is not desirable.

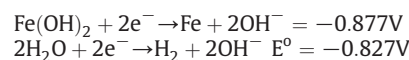
The chemistry of the iron–air rechargeable battery is well-studied. Table 4 lists the limitations of the iron–air battery with respect to round-trip efficiency and cycle life and the underlying technical issues.

#### 3.2. Efficiency

The iron electrode also undergoes self-discharge by reaction with the electrolyte and evolves hydrogen according to the following chemical reaction:



Further, the standard reduction potential for the iron electrode reaction is more negative to that of the hydrogen evolution reaction in alkaline medium.



Consequently, during charging, hydrogen is evolved in addition to the production of iron from iron hydroxide. The faradaic efficiency of

**Table 4**  
Summary of performance issues with the iron–air battery.

Performance limitations of state of art iron air battery	Performance loss in state-of-art technology	Underlying causes of performance loss
Low round-trip energy efficiency	50% round-trip energy efficiency 20% loss of capacity in 14 days	<ul style="list-style-type: none"> <li>Voltage losses during charge and discharge of the oxygen electrode to the extent of 0.5V</li> <li>Self-discharge reaction resulting reaction of the electrolyte with the iron electrode to produce hydrogen</li> </ul>
Cycle life	10% loss in faradaic charge efficiency Limited to 1000–2000 cycles	<ul style="list-style-type: none"> <li>Evolution of hydrogen during charge</li> <li>Electro-oxidation of carbon substrate limits air electrode to 1000 cycles</li> <li>Flooding of electrodes</li> <li>Carbonation of the electrolyte</li> </ul>

the iron electrode is as low as 50%. A considerable loss of efficiency and electrolyte occurs if the evolved hydrogen is left unutilized.

At the air electrode, for current densities of 25–30 mA/cm<sup>2</sup> on charge/discharge, the voltage difference between charge and discharge is 0.5 V. This difference in charge/discharge voltages arises mainly from the activation polarization losses at the air electrode. This voltage loss contributes significantly to the low round-trip efficiency of 50%. While the current densities are higher than what would be used for discharge of batteries for grid-scale electrical storage, the voltage efficiency loss at the air electrode is a significant issue.

### 3.3. Cycle life

The iron electrode is one of the most robust electrodes known to battery electrochemists. The iron electrode has been shown to withstand over 3000 cycles with no significant degradation in nickel–iron batteries. Unlike zinc electrodes, the iron electrode does not suffer from shape change upon cycling and is also extremely tolerant to overcharge and over-discharge.

The air electrode is limited to about 1000 cycles as repeated charge and discharge results in the degradation of the electrode materials and structures. Carbon is typically the support material for the catalysts used in the air electrode. During charging, this carbon support undergoes electro-oxidation resulting in the loss of hydrophobicity and mechanical integrity of the electrode thereby leading to flooding and loss of performance. Further, potassium carbonate formed by the reaction of carbon dioxide present in air with the electrolyte leads to blocking of pores and increases the barrier to transport of oxygen and consequent loss of performance.

## 4. Materials solutions to address the limitations of the iron–air battery

The improvements in round trip efficiency from 50% to 80% can be achieved by:

- reducing the voltage losses at the cathode during charge and discharge
- increasing the faradaic efficiency during charge.
- suppressing the self-discharge of the iron electrode

The actual target values for the voltage losses and faradaic efficiency and round trip efficiency are listed in Table 5.

The improvements in cycle life from 2000 to 5000 cycles can be achieved by:

- avoiding the oxidation of the catalyst structures used at the air electrode
- avoiding carbonation of the electrolyte
- designing electrode structures that stay hydrophobic when subjected to bifunctional operation

The specific material advances required are:

- (1) Selective inhibitors of the hydrogen evolution reaction on iron
- (2) Low-cost efficient bi-functional electrocatalysts for the air electrode

- (3) Low-cost oxidation resistant air electrode materials
- (4) Electrode structures that are resistant to flooding during bifunctional operation
- (5) Methods of avoiding carbonation of the alkaline electrolyte

Some of these material requirements are also shared with the technology of alkaline membrane fuel cells and electrolyzers.

The more challenging material advances are in the area of electrocatalysts. Stable catalysts for oxygen evolution and oxygen reduction in alkali have been studied for many decades, but a bifunctional air electrode catalyst is less studied. Perovskite and pyrochlore oxides have the potential of meeting this requirement. The rich variety in the combination of A and B site metal atoms that can be combined makes the search for an improved catalyst very encouraging. However, a rational approach to catalyst design in this area is still lacking [12]. Materials such as lanthanum cobalt oxide, nickel cobalt oxide spinel and bismuth iridium pyrochlore have been found to be very promising as catalyst materials in the context of other metal–air batteries and electrolyzers [13]. However, the bifunctional properties of these electrodes must be developed. Their performance can be optimized for operation at low current densities, because the grid storage applications will be able to tolerate a much lower rate than transportation applications.

The challenge of an inexpensive air electrode that is robust towards oxidation is also common to polymer electrolyte membrane (PEM) fuel cells. Fortunately, progress in this arena is favored by the alkaline electrolyte of the iron–air cell because more materials are compatible with this chemistry than with the acidic electrolyte of the PEM cell. Nitrides and carbides of transition metals can serve as robust substrates [9]. Organic materials such as pyrolyzed macrocycles can serve as oxidatively stable substrates. Nanostructures based on substrates that are robust to oxidation will be attractive for dispersing the catalysts.

The operation of the bifunctional air electrode is accompanied by the transport of hydroxide ions and electro-osmotic drag of water molecules. The direction of the electro-osmotic drag of water is reversed when the air electrode switches between oxygen evolution and oxygen reduction reaction. An interface that must stay flooded during oxygen evolution and at the same time relatively “dry” and capable of diffusing gasses to allow for efficient electro-reduction of oxygen is a major design challenge for maintaining the robustness of the air electrode. Westinghouse Corporation has researched multi-layer structures to address this problem [9]. However, in principle, with the use of wettable ionomer coatings, non-wettable additives that are stable under oxidation conditions, and a thin electrode structure with a very short path length for gas diffusion, an appropriate balance in water and gas transport can be achieved.

Suppressing the hydrogen evolution reaction at the iron electrode may be approached via additives to the electrode or to the electrolyte. Finding an additive that will selectively suppress the hydrogen evolution reaction without affecting the kinetics of the battery electrode reaction is the principal challenge. The additive has to be stable at the negative electrode potentials of the iron electrode. Also, the additives to the electrolyte must be stable towards oxidation at the air electrode and must not impair the kinetics of the air electrode reactions.

**Table 5**  
State-of-Art and target values for the development of the iron–air battery for grid-scale energy storage applications.

Parameter	State-of-Art	Target
Voltage losses during charge (cathode)	300 mV	150 mV
Voltage losses during discharge (cathode)	200 mV	100 mV
Faradaic charge efficiency	90%	96%
Loss of efficiency by self discharge per day	1–2%	0.1%
Thermodynamic voltage corresponding to 100% efficiency	1.28	1.28
Overall round trip efficiency	$(1.28 - 0.2) * 0.9 / (1.28 + 0.3) - 1\% = 60\%$	$(1.28 - 0.1) * 0.96 / (1.28 + 0.15) - 0.1\% = 80\%$

Additives to the electrode must be insoluble enough to last for 15 years. Sulfide additives have been used in the iron electrode to reduce hydrogen evolution but their benefit is not always clear. While sulfides improve the discharge and charge rates, their ability to reduce hydrogen evolution is dependent on the type of metal sulfide used [7]. In choosing these additives, materials such as bismuth sulfide are particularly promising because of the non-toxicity of bismuth compounds relative to lead and cadmium.

The selection of raw materials for the fabrication of the iron electrode is very important in the suppressing the hydrogen evolution reaction. Impurities in the oxide precursors can promote the evolution of hydrogen, because transition metals such as manganese and nickel have lower overvoltage for hydrogen evolution compared to iron. Historically, iron electrodes have been fabricated from magnetite and hematite minerals. While these have a tremendous cost advantage, further purification of these minerals will improve the faradaic efficiency.

Another approach to addressing the challenge of faradaic efficiency is to utilize the hydrogen produced in the reaction. Designing electrode structures that can capture the hydrogen and utilize it will result in improved efficiency. This type of hydrogen capture requires new material architectures that must be carefully chosen so as not to increase the cost of fabrication of the iron electrodes.

Avoiding carbon dioxide access to the electrode is a direct method of preventing degradation due to carbonation of the electrolyte. Identifying a low-cost carbon dioxide absorber that can be regenerated without much energy expenditure is a principal area for development. This problem is shared with the larger area of carbon sequestration and utilization.

## 5. Conclusions

The preliminary assessment of the advantages and features of the iron–air battery shows that this technology can be a promising candidate for grid scale energy storage applications. The faradaic efficiency of the iron electrode, voltage efficiency of the air electrode and the

durability of the air electrode must be improved to meet the energy efficiency and cycle life requirements for grid-scale deployment. Using additives in the electrode and electrolyte is a viable direction for suppressing the hydrogen evolution at the iron electrode. Since suppressing hydrogen evolution completely is going to be difficult, utilizing the hydrogen through the use of a modified iron electrode structure is also a promising direction. Increasing the oxidative stability of the air electrode will need more robust catalyst supports. The bifunctional air electrode that is stable for 5000 h of operation requires further optimization of the perovskite and pyrochlore oxides for catalytic activity and stability.

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